Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22023

105 (2018) 132–143
February

Efficiency analysis of electro-Fenton combined with coagulation process for the degradation of natural rubber latex processing and production waste waters using bench-scale reactor

S. Devi[a], S. Adishkumar[b,*], J. Rajesh Banu[c]

[a]*Department of Civil Engineering, Government Polytechnic College, Thoothukudi, India, Tel.+91 9940214464, email: devi_ selvaraj07@yahoo.co.in (S. Devi)*
[b]*Department of Civil Engineering, University V.O.C College of Engineering, Anna University, Thoothukudi Campus, Thoothukudi, India, Tel. +91 9841339016, Fax 0462-2552877, email: adishk2002@yahoo.co.in (S. Adishkumar)*
[c]*Department of Civil Engineering, Regional Campus of Anna University, Tirunelveli, India, email: rajeshces@gmail.com (J.R. Banu)*

Received 17 June 2017; Accepted 12 February 2018

ABSTRACT

Degradation of latex wastewater contaminated with a mixture of organic compounds has become a unique challenge among the researchers. An effort was initialized to treat the latex wastewater using electro-Fenton process followed by coagulation. Wastewater collected from the natural rubber latex processing and production industries were treated using bench scale reactor with hopper bottom of 5 L working volume equipped with iron anode and graphite cathode and the effect of COD and colour removal were studied. Response surface methodology based on central composite design (CCD) was performed to evaluate the optimal values of parameters such as pH, Fe^{2+} concentration, H_2O_2 concentration and current intensity of electro-Fenton process. In latex processing wastewater, 82% COD removal and 92% colour removal were achieved in 30 min reaction with an optimal values of pH-3.5, Fe^{2+} –573 mg/L and H_2O_2 –7424 mg/L. In case of latex production wastewater, COD removal and colour removal were 85% and 91% corresponds to an optimal values of pH –4.1, Fe^{2+} –378 mg/L and H_2O_2 –3170 mg/L. The worked out operational cost per kg of COD reduction were 7 $ and 8.5 $ for production and processing wastewater respectively. The results obtained revealed that electro-Fenton process could be a valuable treatment against the conventional treatment methods for latex wastewater.

Keywords: Latex wastewater; Coagulation; Electro-Fenton; Bench-scale reactor; Iron anode; Graphite cathode; Response surface methodology; CCD.

1. Introduction

Modernization and developmental activities in India increases the usage of rubber products day by day. In order to meet out the increasing demand on rubber products, there is a considerable development in the rubber processing industries. Rubber processing industries uses high toxic chemical substances and enormous amount of water for the production of rubber products which in turn generates huge quantity of wastewater [1–3]. The raw wastewater emanating from rubber manufacturing plants contains toxic pollutants; it cannot be disposed off to the environment directly and necessitates treatment of wastewater [1]. Moreover considering the scarcity of water resources, most of the industries have adopted the process of recycling wastewater. As explained above, evolving cost-effective treatment of wastewater is an essential requirement for natural rubber processing industry.

The latex is a white milky substance obtained from the tree, *Hevea brasiliensis*. Fresh latex, as it comes out from the tree, is slightly alkaline or neutral. It turns acidic rapidly due to the bacterial action. Therefore, fresh latex cannot be kept for long time without precoagulation. Ammonia, sodium sulphite and formalin are used as anticoagulants for preserv-

---

*Corresponding author.

1944-3994 / 1944-3986

ing the fresh latex [4]. The field latex can then be processed to primary rubber products such as concentrated latex (raw material for medical gloves and balloons), block rubber (raw material for high viscosity products such as soles and belts), and ribbed smoked sheet rubber (raw material for vehicle tyres and industrial rubber parts) in processing sector industries and then subsequently processed to different final rubber products in production sector industries [3,5,6].

A large quantity of water is used in rubber latex processing for washing, dilution of the latex and in further processing steps. Consequently a quite large amount of wastewater, including also that obtained for washing of floor, machines and cleaning tanks and serum generally will be discharged to receiving waters [7]. This wastewater contains a certain quantity of uncoagulated rubber particles and a quite high content of soluble pollutants, e.g. acetic/formic acid, sugars, proteins, lipids, carotenoids, inorganic and organic salts [1,8,9]. These pollutants obviously affect quite adversely the ecology and the health of people living in the surrounding environment. The main pollution problems caused by rubber latex processing wastewater concern the discharge of substantial amounts of biodegradable organic compounds and the offensive smell of the wastewater.

Hence, the wastewater generated from the rubber industries cannot be discharged into the environment without proper treatment. Plant details under Indian scenario shows that volume of wastewater generated from such category of industry varies ranging from 15 to 40 L/kg of latex consumed [7]. Generally, conventional biological processes such as lagoon system, oxidation ditch, anaerobic digestion and activated sludge processes are adopted for the treatment of natural rubber processing in India [1,10–12]. Existing biological treatment methods for treating latex wastewater faced major drawbacks as it takes longer retention time for the degradation of pollutants and it has limitation with the degradation of non-biodegradable organics present in the wastewater and in addition, it requires large areas [12,13].

Electro-Fenton processes have progressively become an eye-catching alternative to the conventional advanced oxidation process and applied for treating various synthetic and real waste waters [14]. Fenton process is a homogeneous reaction and is environmentally acceptable which involved the use of two chemicals namely hydrogen peroxide (H_2O_2) as the oxidant and Ferrous ion as the catalyst at acidic pH. The $HO^{\cdot}$ generated is capable to detoxify the contaminants via oxidation. In the electro-Fenton process, hydroxyl radicals are produced electrochemically at the cathode from the Fenton's reagent (Fe^{2+} and H_2O_2) [Eq. (1)]. The Fe^{2+} is generated by passing of direct current between suitable electrodes through the electrochemical dissolution of anode [Eq. (2)] [15] and thus reduces the requirement of addition of iron salt [15]. Even if the solubility of oxygen is poor, H_2O_2 can be electrochemically generated [Eq. (4)] at a cathode, when the cathode is made of carbonaceous materials through dissolved oxygen in the system and may be through discharge of oxygen at the anode [Eq. (3)] [16–19]. Since the rate of generation of H_2O_2 was limited to the Fe^{2+-} generation, it was supplemented externally. If there are Fe^{3+} species in the medium, they revert to Fe^{2+} by reducing H_2O_2 or organic intermediate radicals [Eq. (5)], or by direct reduction of Fe^{3+} on the cathode [Eq. (6)] [20,21]. Therefore hydroxyl radicals and hydroperoxyl radicals generated at anode and cathode degrades the organic pollutants, while most of the degradation is by the stronger oxidizing power of hydroxyl radicals [22]. The residual Fe ions get precipitated through coagulation [Eqs. (7), (8)] [23,24].

$$\mathrm{Fe}^{2+} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^{-} + \mathrm{OH}^{\cdot} \quad (1)$$

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (2)$$

$$2\mathrm{H_2O} \rightarrow 4\mathrm{H}^{+} + \mathrm{O_2} + 4\mathrm{e}^{-} \quad (3)$$

$$\mathrm{O_2} + 2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H_2O_2} \quad (4)$$

$$\mathrm{Fe}^{3+} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe-OOH}^{2+} \rightarrow \mathrm{Fe}^{2+} + \mathrm{HO}_2^{\cdot} \quad (5)$$

$$Fe^{3+} + e \rightarrow Fe^{2+} \quad (6)$$

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \quad (7)$$

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3 \quad (8)$$

Since the oxidation power of hydroxyl radicals is 2.8 eV, the rate of degradation of organic pollutants is incredibly higher than the conventional treatment methods. Particularly, electro-Fenton method, wherein Fenton's oxidation and electro coagulation are carried out in concert, yields substantially good results in the treatment of high strength waste waters. This is a focal point in electro-Fenton process [17]. Electro-Fenton process has been applied to treat various waste waters and the operational efficiency of process was listed in Table 1. As per open literature available, the performance analysis of electro-Fenton process for latex wastewater has not been reported. Hence an attempt has been initiated to study the effectiveness of electro-Fenton process for the treatment of latex wastewater.

2. Materials and methods

2.1. Materials

All chemicals were commercially available analytical grade reagents and used as received without further puri-

Table 1
Operational efficiency of electro-fenton process on various wastewater

Wastewater	Operational efficiency	Electrolysis time	Reference
Pesticides	>90% TOC removal	8 h	20
Rayon Industry	88% COD removal	50 min	15
Dyes	98% Decolourisation	30 min	21
Real dye	75% COD removal	240 min	34
Landfill leachate	82% TOC removal	6 h	14
	94% COD removal	43 min	42
Poultry	88% COD removal	30 min	41
Petrochemical	68% COD removal	73 min	45

fication. Sodium hydroxide, sodium sulfate, sulfuric acid, hydrogen peroxide (30%, w/v), ferrous sulfate heptahydrate and all other reagents were purchased from Merck. All solutions were prepared by dilution with deionized water to the desired concentrations and experiments were performed at room temperature.

2.2. Collection and characterization of wastewater

The study was conducted into an industrial waste water of latex processing and production industries obtained from ribbed smoke sheet processing industry at Thirparappu and from a gloves production industry located at Kavalkinaru of Kanyakumari District, Tamil Nadu, India. The characteristics of latex processing and production industries wastewater is presented in Table 2. The results obtained through characteristics analysis shown that the pH and the COD value of processing industry wastewater was 3.5 and 14200 mg/L and production industry wastewater was 3.4 and 5100 mg/L. The acidic nature of collected wastewater made an ideal environment for electro-Fenton process. The collected wastewater was preserved at a temperature less than 4ºC, but was above the freezing point in order to prevent the wastewater from undergoing biodegradation due to microbial action [11,12].

2.3. Electro-fenton reactor and procedures

The electro-Fenton experiments in this study were carried out using bench scale reactor made with acrylic material and hopper bottom of 21.5 cm × 15 cm × 25 cm with a working volume of 5 L. The reactor was equipped with graphite plate cathode (212 cm^2) and iron plate anode (171 cm^2). The two parallel electrodes were arranged with 6 cm spacing. The electrodes were connected to a DC power supply (0–30 V, 0–5 A) to provide the desired current. The photograph of the experimental setup is shown in Fig. 1. Electrodes were cleaned with emery paper (No. P320) between the successive runs and then washed with H_2SO_4 solution (5% v/v) to reduce the effects on proceeding experiments [15].

The wastewater was allowed to settle for 60 min. After sedimentation, initial pH of the solution was adjusted to the desired values using concentrated sulphuric acid or sodium hydroxide before adding Fenton reagents. In each run, a pre-decided amount of ferrous sulphate heptahydrate and hydrogen peroxide were added into the reactor to activate Fenton's reaction before the electrical current was turned on. Samples of 5 ml volume were withdrawn every 10 min and immediately the pH of the sample was adjusted to 11 using NaOH and sodium sulphite to quench the generation of $^{\cdot}OH$ and terminate the degradation process and to precipitate remaining iron [14,15,25–27]. The samples were allowed to stand 30 min settling time for coagulation and the supernatant was then taken for quality measurements [17]. The COD of the samples were determined by the standard dichromate open reflux method [28]. The sludge content was quantified using imhoff cone apparatus [29]. The removal of colour was evaluated by determining the absorbance of the solution at λ = 460 nm using UV–Vis spectrophotometer [30,31].

Table 2
Characteristics of wastewater after plain sedimentation

Parameter	Latex processing wastewater	Latex production wastewater
pH	3.5 ± 0.10	3.4 ± 0.12
COD (mg/L)	14200 ± 400	5100 ± 200
BOD (mg/L)	1965 ± 100	785 ± 140
Colour	Pale white	yellow
Total solids (mg/L)	30125 ± 500	10425 ± 180

3. Results and discussions

3.1. Experimental design, regression models and statistical testing

Response surface methodology was employed for the experimental design and optimization with the software Design Expert (version 10.0.6, trial). It was used to determine the relationship between the electro-Fenton process responses (COD and colour removals) with the most important variables (wastewater pH, Fe^{2+} dosage, H_2O_2 dosage and applied current intensity). The rotatable experimental plan was carried out as a central composite design (CCD) consisting of 30 experiments. For four variables ($n = 4$) and five factor levels (low (–), middle (0), and high (+)), the total number of experiments was 30 determined by the expression: 2^n ($2^4 = 16$: factor points) + 2n (2 × 4 = 8: axial points) + 6 (center points: six replications). The ranges and the levels of the variables investigated in this study are given in Table 3. A complete set of the experimental design is shown in Table 4. As shown in Table 3, the five-level CCD was implemented to investigate the effects of four independent operating variable conditions [X1 (pH: 2–6), X2 (Fe^{2+} dosage: 0–1190 mg/L), X3 (H_2O_2 dosage: 0–11900 mg/L), and X4 (current: 0.1–0.5 A)] on the responses Y1 and Y2 [% of COD removal (Y1), % of Colour removal (Y2)]. The following second-order model [Eq. (9)] attains the correlations between the responses and the independent variables.

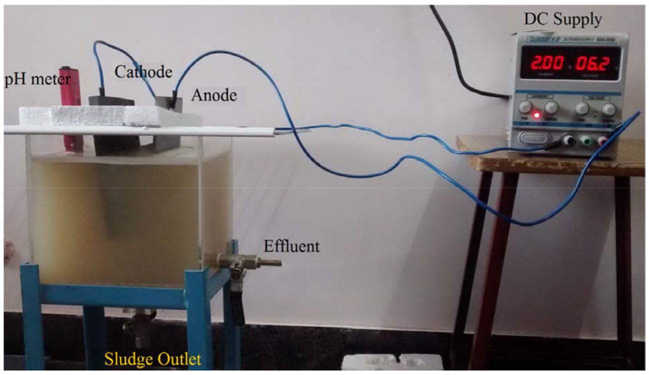

Fig. 1. Photograph showing the experimental setup of electro-Fenton process.

Table 3
Independent variables and their levels obtained from the statistical software

Symbol	Factor	Coded levels of variables		
		−2	0	+2
X1	pH	2	4	6
X2	Fe^{2+}	0	595	1190
X3	H_2O_2	0	5950	11900
X4	Current intensity	0.1	0.3	0.5

Table 4
Experimental matrix design for electro-Fenton process

Std	Run	Space type	Factor 1	Factor 2	Factor 3	Factor 4
			A:pH	B:Fe^{2+}	C:H_2O_2	D:Current
				mg/l	mg/l	A
26	1	Center	4	595	5950	0.3
5	2	Factorial	3	297.5	8925	0.2
24	3	Axial	4	595	5950	0.5
17	4	Axial	2	595	5950	0.3
9	5	Factorial	3	297.5	2975	0.4
16	6	Factorial	5	892.5	8925	0.4
1	7	Factorial	3	297.5	2975	0.2
7	8	Factorial	3	892.5	8925	0.2
25	9	Center	4	595	5950	0.3
29	10	Center	4	595	5950	0.3
19	11	Axial	4	0	5950	0.3
18	12	Axial	6	595	5950	0.3
11	13	Factorial	3	892.5	2975	0.4
3	14	Factorial	3	892.5	2975	0.2
4	15	Factorial	5	892.5	2975	0.2
22	16	Axial	4	595	11900	0.3
23	17	Axial	4	595	5950	0.1
28	18	Center	4	595	5950	0.3
10	19	Factorial	5	297.5	2975	0.4
14	20	Factorial	5	297.5	8925	0.4
12	21	Factorial	5	892.5	2975	0.4
21	22	Axial	4	595	0	0.3
6	23	Factorial	5	297.5	8925	0.2
20	24	Axial	4	1190	5950	0.3
8	25	Factorial	5	892.5	8925	0.2
2	26	Factorial	5	297.5	2975	0.2
15	27	Factorial	3	892.5	8925	0.4
13	28	Factorial	3	297.5	8925	0.4
30	29	Center	4	595	5950	0.3
27	30	Center	4	595	5950	0.3

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{i<j} \beta_{ij} x_i x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \varepsilon \tag{9}$$

where Y is the response, β_0 is a constant coefficient, β_j, β_{jj} and β_{ij} are linear, quadratic and interactive effects coefficients respectively. x_i and x_j are coded levels for the independent variables. k is the number of independent variables and ε is the random error. Reduced models for describing the COD and Colour removal after excluding the insignificant coefficients is presented below for latex processing wastewater [Eqs. (10), (11)] and latex production wastewater [Eqs. (12), (13)].

Latex Processing wastewater

$$\begin{aligned} Y1_1 &= 78.41 - 4.66A - 2.32B + 5.23C + 1.61D \\ &-3.59AB - 3.32AC - 5.18AD - 4.68BD - \\ &1.28CD - 7.07A^2 - 4.93B^2 - 5.11C^2 - 5.40D^2 \end{aligned} \tag{10}$$

$$\begin{aligned} Y2_1 &= 88.05 - 6.69A - 2.48B - 1.13C \\ &+2.67D + 0.83AB + 0.94CD - 1.29A^2 \\ &-1.16C^2 - 1.88D^2 \end{aligned} \tag{11}$$

Latex production wastewater

$$\begin{aligned} Y1_2 &= 82.64 + 2.86A - 5.13B + 2.00AC - \\ &3.49AD - 12.22BD - 9.98CD - 5.51A^2 \\ &-5.47B^2 - 8.63C^2 - 8.86D^2 \end{aligned} \tag{12}$$

$$\begin{aligned} Y2_2 &= 86.22 - 4.36A - 2.65B - 1.10C + \\ &2.41D - 2.31AD + 3.77BC - 1.90A^2 \\ &-1.\ 52C^2 - 3.28D^2 \end{aligned} \tag{13}$$

The COD and colour removal values obtained from the experiments (observed) and Eqs. (10)–(13) (predicted) are publicized in Table 5. The adequacy of the model includes some assessments for regression model consideration. It produces statistics such as F-values, p-values, and R-squared values for comparing the models. Analysis of variance (ANOVA) was carried out and the results were shown in Table 6, for this purpose. The determination coefficient (R^2) represents the goodness-of-fit for the model. When R^2 is close to 1, the response can be appropriately predicted by the model. High correlation coefficients $R^2 > 0.94$, R^2 adjusted > 0.89 and R^2 predicted > 0.75 for all responses as shown in Table 6 means that the regression model fits to the experimental value and it can afford an excellent explanation of interaction among the independent variable and the response. The model was considered to be statistically significant as the Prob > F (p-values) values from the ANOVA were less than 0.05. All models of this study showed that values of Prob > F were <0.0001 as in Table 6. The Fischer's F-statistics values (F-values) were 44–81 for COD removal and 19–67 for colour removal. The large F-values and smaller the value of p for all responses represented that most of the variation in the response could be explained by the regression model. The coefficient of variance (CV) as the ratio of the standard error of estimate to the mean value of the observed response (as a percentage) was a measure of reproducibility of the model and also CV was considered to be reproducible when it is not greater than 10%. As shown in Table 6, from the values of CV the model can be considered reasonably reproducible. The adequate precision (AP) measures the signal to noise ratio and it was compared for the range of the predicted values at

Table 5
Observed (actual) and predicted data for electro-Fenton process

Run	Latex processing wastewater				Latex production wastewater			
	COD removal		Colour removal		COD removal		Colour removal	
	Act.	Pred.	Act.	Pred.	Act.	Pred.	Act.	Pred.
	%	%	%	%	%	%	%	%
1	78.93	78.41	86.13	88.05	82.64	82.64	88.35	86.22
2	56.61	58.05	89.65	88.17	48.71	47.89	77.42	79.05
3	60.08	60.04	85.54	85.88	43.00	45.29	79.31	77.92
4	57.96	59.46	94.15	96.27	52.00	54.89	88.68	87.34
5	63.41	63.11	97.15	96.60	89.29	84.34	94.61	97.39
6	36.00	37.31	77.79	77.70	27.29	27.92	76.07	74.67
7	38.94	37.60	93.61	92.95	34.43	34.84	86.64	86.06
8	70.73	69.16	81.52	81.67	66.46	65.11	82.18	80.80
9	78.70	78.41	88.79	88.05	86.21	82.64	87.80	86.22
10	78.70	78.41	87.87	88.05	79.96	82.64	83.53	86.22
11	63.20	63.34	89.98	91.45	70.14	71.01	93.61	93.48
12	41.35	40.82	70.37	69.52	66.57	66.34	70.64	69.92
13	57.45	57.06	91.06	89.90	48.43	47.82	82.76	82.12
14	51.34	50.28	86.00	84.93	48.71	47.21	70.37	72.72
15	49.39	50.81	74.02	74.18	55.86	55.31	71.51	71.88
16	69.00	68.41	81.20	81.16	48.71	47.62	77.44	77.93
17	52.59	53.61	74.27	75.20	48.71	49.08	68.97	68.30
18	78.70	78.41	88.08	88.05	81.75	82.64	87.16	86.22
19	55.71	57.24	81.74	80.85	77.29	79.69	84.99	84.39
20	59.17	59.28	79.04	79.58	63.00	60.79	70.22	71.92
21	39.24	36.85	76.49	77.44	44.86	41.97	69.64	72.06
22	45.92	47.50	84.37	85.68	44.86	48.62	84.89	82.33
23	59.26	59.62	73.45	73.87	63.53	65.19	73.03	71.69
24	53.22	54.06	81.74	81.54	48.71	50.50	84.83	82.89
25	57.04	56.39	70.64	70.67	79.96	81.20	75.10	76.37
26	54.08	52.46	79.58	78.90	46.64	44.15	81.20	82.29
27	70.15	70.82	90.25	90.41	27.00	25.78	85.36	88.32
28	79.89	78.44	96.50	95.59	55.86	57.45	90.86	88.50
29	78.70	78.41	89.54	88.05	84.42	82.64	83.75	86.22
30	76.70	78.41	87.87	88.05	80.85	82.64	86.73	86.22

Table 6
Quadratic model ANOVA results for electro-Fenton process

Variable	Latex processing wastewater		Latex production wastewater	
	COD	Colour	COD	Colour
Standard deviation	1.55	1.31	2.88	2.39
Mean	60.41	84.28	59.86	81.26
R2	0.993	0.984	0.987	0.948
R^2 adjusted	0.987	0.970	0.975	0.899
R^2 predicted	0.963	0.927	0.937	0.756
Coefficient of variance (CV)	2.56	1.55	4.81	2.94
Press	191.38	119.41	598.09	399.15
Adequate precision	38.04	29.31	28.79	17.24
F-value	44.43	66.81	80.69	19.45
Prob > F	<0.0001	<0.0001	<0.0001	<0.0001

the design points to the average prediction error. The AP values greater than 4 indicate an adequate signal for all responses. Therefore by considering the above facts, the quadratic model could be used to follow the design space defined by CCD for electro-Fenton process.

3.2. Response surface plotting

3D plots for all the process from the response surface software are shown in Figs. 2 and 3 to visualize the effects of experimental factors on removal effi-

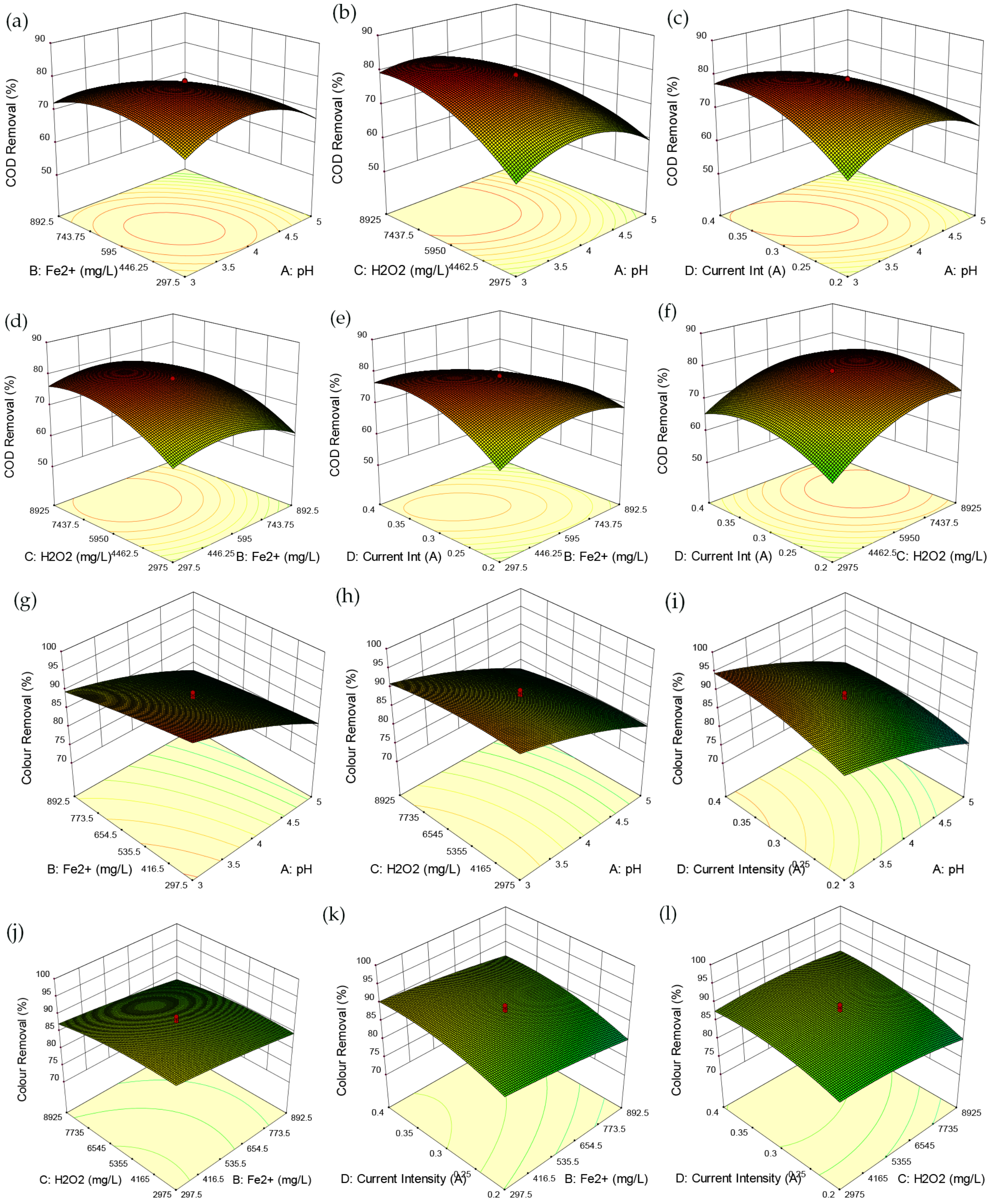

Fig. 2. Effect of variables on COD and colour removal in Latex processing wastewater: (a) pH and Fe^{2+}, (b) pH and H_2O_2 (c) pH and current intensity, (d) Fe^{2+} and H_2O_2, (e) Fe^{2+} and current intensity, (f) H_2O_2 and current intensity for COD removal, (g) pH and Fe^{2+}, (h) pH and H_2O_2, (i) pH and current intensity, (j) Fe^{2+} and H_2O_2, (k) Fe^{2+} and current intensity, (l) H_2O_2 and current intensity for colour removal.

ciencies of COD and Colour. Some interactions among variables were significant. The optimum conditions for maximum values of the responses are attributed to all variables.

3.3. Optimization and validation

Numerical optimization will optimize any combination of one or more responses. It was used to determine the maximum degradation and decolorization of the electro-Fenton

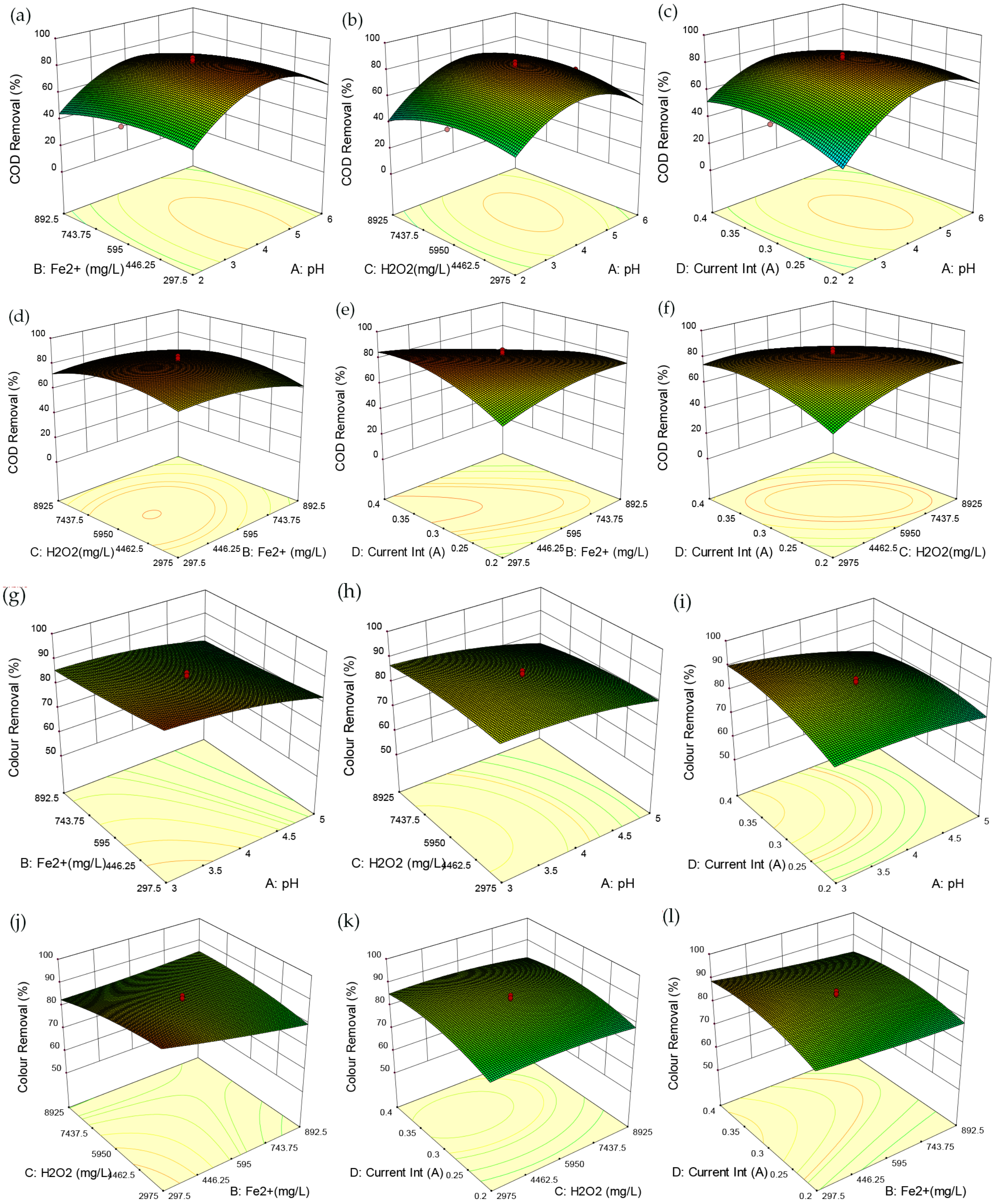

Fig. 3. Effect of variables on COD and colour removal in Latex Production wastewater : (a) pH and Fe^{2+}, (b) pH and H_2O_2 (c) pH and current intensity, (d) Fe^{2+} and H_2O_2, (e) Fe^{2+} and current intensity, (f) H_2O_2 and current intensity for COD removal, (g) pH and Fe^{2+}, (h) pH and H_2O_2, (i) pH and current intensity, (j) Fe^{2+} and H_2O_2, (k) Fe^{2+} and current intensity, (l) H_2O_2 and current intensity for colour removal.

process parameters. Based on response surface and desirability functions, the optimum conditions for COD and colour removals were obtained and experimental verification is shown in the Table 7.

The initial pH value of the wastewater has a significant effect on the electro-Fenton process. It affects the speciation of iron and decomposition of H_2O_2 [32]. The reductions in COD and colour removal efficiency of electro-Fenton process with respect to pH are shown in Figs. 2 and 3a–c and 3g–i. As illustrated in Table 7, the optimum pH for electro-Fenton was 3.5 for latex processing wastewater at a maximum of 82% COD removal and 92% colour removal. And it was achieved as 4.1 for latex production wastewater at a maximum removal of 85% COD removal and 91% colour removal. When the pH rises from 2.0 to 4.0, COD removal increases from 60% to 78% for latex processing wastewater as shown in Figs. 2a and 2g. The COD removal increases from 55% to 82% for latex production wastewater as illustrated in Figs. 3a and 3g. It was identified that a high concentration of H^+ is needed for the generation of hydrogen peroxide [Eq. (4)] [33]. Moreover, there is a possibility for the formation of hydrogen at very low pH which could consumes the active sites for the production of hydrogen peroxide [Eq. (14)] which will in turn reduces the COD removal percentage [33–35]. When the pH increases, the COD removal increases due to the presence of more H^+ ions for the generation of H_2O_2 [Eq. (4)]. In addition at low pH, catalyst Fe^{2+} is deactivated since iron species form stable complexes with hydrogen peroxide [34–37].

$$2H^+ + 2e^- \rightarrow H_2 \tag{14}$$

As shown in Figs. 2a and 2g, when the pH rises from 4.00 to 6.00, COD removal and colour removals respectively decreases from 78% to 41% and from 88% to 70% for the latex processing wastewater. From Figs. 3a and 3g, COD removal and colour removal decreases from 82% to 51% and from 86% to 70% respectively for the latex production wastewater. It has been observed that from the results obtained, when pH value rises from 4 to 6 affects the electro-Fenton reaction and it invariably reduces the COD removal efficiency due to the transformation of ferrous ions into ferric ions [Eqs. (15) and (16)], and in succession to ferric hydro complexes or ferric oxy hydroxide [Eq. (17)] [38]. Also higher the pH value develops the reaction between ferrous ion and hydroxyl ion which will turn precipitates ferric hydroxide [Eq. (7)] and thereby affects the efficiency of the electro-Fenton process considerably [33].

$$HO_2^{\cdot} + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \tag{15}$$

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^- \tag{16}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow FeOOH^{2+} + H^+ \tag{17}$$

At pH > 5, H_2O_2 becomes unstable and itself quickly decomposes into O_2 and H_2O, thus losing its oxidation potential [33,36]. At pH < 3, H_2O_2 become very unstable and tends to use up a proton to produce oxonium ion [Eq. (18)] [39]. An oxonium ion enhances its stability by making peroxide electrophilic, leads to the reduction of reactivity with the catalyst [18,33,36,40].

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{18}$$

Furthermore at acidic medium between pH 3 and 5, the Fe^{2+} and H_2O_2 would remain stable and they exists. As a result, a strong reaction of Fenton can happen under these conditions [36]. Thus the optimum pH values of 3.5 and 4.1 would be more distinct to decompose the H_2O_2 to hydroxyl radicals by Fe^{2+} ions.

The applied current density is the most important parameter in electro-Fenton process, its value is crucial for the operational cost and process efficiency. The applied current act as a driving force to generate oxidized iron (Fe^{2+}) at an anode and the other side it generates H_2O_2 at cathode through oxygen reduction. Fe^{2+} produced at anode reacts with H_2O_2 and produces hydroxyl radical which reduces the complex species of the latex wastewater. Moreover the generation of Fe^{2+} at anode has to be proportionate to the H_2O_2 generated at cathode to get the optimum efficiency. To utilize the current intensity effectively for the treatment of latex wastewater, current intensity range from 0.1 to 0.5 A (4.7 to 23.58 A/m^2 current density) was chosen and obtained results on COD reduction and colour reduction are represented graphically in Figs. 2 and 3c, e, f and i, k, l. As illustrated in Table 7, the optimum current intensity for COD and colour removals are 0.34A (16.04 A/m^2) and 0.39A (18.39 A/m^2) for latex processing wastewater and latex production wastewater respectively.

As shown in Figs. 2c and 2i, when the current intensity rises from 0.10 to 0.40 A, COD removal and colour removals respectively increases from 54% to 78% and from 75% to 88% for latex processing wastewater, whereas in the case of latex production wastewater, COD removal and colour removals respectively increases from 49% to 83% and from 68% to 86% as represented in Figs. 3c and 3i. Further increase of current intensity above 0.40A exhibit competitive reaction such as discharge of oxygen at anode [Eq. (3)] and evolution of hydrogen [Eq. (14)] at cathode may takes place [35,38,41,42]. Due to these reactions at higher current,

Table 7
Optimum conditions found by design expert and experimental verification for electro-Fenton process

WW	pH	Fe^{2+}	H_2O_2	Current intensity	COD removal		Colour removal	
					Observed	Predicted	Observed	Predicted
		mg/l	mg/l	A	%	%	%	%
Latex processing wastewater	3.5	573	7424	0.34	81.25	81.83	90.5	91.86
Latex production wastewater	4.1	378	3177	0.39	84.82	85.12	93.61	90.53

the Fenton reactions are inhibited considerably above 0.4 A. Thus the optimum current intensity of 0.34 A for latex processing wastewater and 0.39 A for latex production wastewater was appropriately suitable for electro-Fenton process.

The production rate of H_2O_2 and Fe^{2+} on electro-Fenton process defines the efficiency of treatment. The electro generation of H_2O_2 and Fe^{2+} mainly depends on the presence of dissolved oxygen in wastewater, the acidic and basic nature of wastewater and intensity of current and types of electrodes used. H_2O_2 production has to be in proportion with Fe^{2+} generation [43]. The values lesser and higher than the proportionate ratio resulted in reduction in efficiency due to the occurrence of advance reaction and production of complex compounds. Hence H_2O_2 and Fe^{2+} were added externally to the wastewater to exhibit effective treatment system.

In this study, to optimize the dosage of H_2O_2, the theoretical H_2O_2 was calculated as suggested by P. Gosh et al. (2011). Based on this H_2O_2 range was fixed as 0 to 11900 mg/L. Since the typical ratio of H_2O_2 and Fe^{2+} is in the range of 10, the Fe^{2+} range is selected as 0 to 1190 mg/L [44]. The experiment was performed at different values of Fe^{2+} and H_2O_2 within the range as mentioned in Table 3 and results obtained are analyzed through RSM. The responses of RSM for Fe^{2+} and H_2O_2 dosage are depicted in Figs. 2 and 3a, b, d–h, j–l.

From Figs. 2 and 3b, h, the COD removal percentage increases with the addition of H_2O_2 dosage up to a value of 5000 mg/L for latex processing and production wastewater and achieved a COD reduction of 78% and 82% respectively. Further increase of H_2O_2 dosage up to a value of 10000 mg/L shows reduction in COD removal from 78% to 72% for latex processing wastewater and it was 82% to 67% in case of latex production wastewater. At higher concentration of H_2O_2 [Eq. (19)], the generation of hydroperoxide radical is predominant which reacts with Fe^{2+} and reduces the generation of hydroxyl radicals [Eq. (15)].

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{19}$$

From Figs. 2 and 3d, j, the COD removal percentage increases with the addition of Fe^{2+} dosage upto a value of 595 mg/L for latex processing and production wastewater and achieved a COD reduction of 78% and 83% respectively. Further increase of Fe^{2+} dosage upto a value of 1190 mg/L shows reduction in COD removal from 78% to 54% for latex processing wastewater and it was 83% to 51% in case of latex production wastewater. The residual Fe^{2+} ions react with hydroxyl ions and forms iron hydroxides [Eqs. (7), (8)] which increase the pH and settle as sludge at the bottom. The increase in pH value considerably affects the Fenton reaction. Beyond the Fe^{2+} dosage of 595 mg/L, the excess Fe^{2+} consumes the effective hydroxyl radicals and produces the iron complexes [Eqs. (5), (17)] results in COD reduction [34,35,40,42]. In addition Fe^{3+} generated as per Eqs. (1) and (16), occupies the active sites and reduces the number of effective sites for the production of H_2O_2 on the cathode surface [34,37]. Thus the optimal condition was attained at the dosage of Fe^{2+} and H_2O_2 were 573 mg/L and 7424 mg/L respectively for latex processing wastewater and for latex production wastewater the values were 378 mg/L and 3177 mg/L respectively as described in Table 7. The sludge produced at optimum condition of reaction was 5.4 mL/L. The increase in pH was observed as +0.1 for every 30 min.

Generally in electro-Fenton process, iron ions are regenerated on the cathode surface [Eq. (6)]. The use of iron electrodes in electro-Fenton process induces the production of Fe^{2+} at the anode surface [Eq. (2)]. The production of Fe^{2+} at anode surface can be calculated from Faraday's law [Eq. (20)] [30,45].

$$m = \frac{MIt}{nF} \tag{20}$$

where m is the mass of substance produced at the electrode, M is the molar mass of substance, I is the total electric charge that passes through the solution, t and n are reaction time and valence number of the substance (as an ion in solution), respectively. F is the Faraday's constant (=96,485 c/mole). It seems that the regeneration and production of iron ions (Fe^{2+}) increases when iron electrodes are used. For the optimal condition the iron ions generated was calculated for latex processing and production wastewater as 177 mg and 203 mg. The additional generation of iron ions reduces the external requirements of Fe^{2+}. Figs. 4 and 5 explain the curtailment of Fe^{2+} requirement and hydrogen peroxide is consumed accordingly.

The performance of electro-Fenton process is assessed based on the energy consumption. The energy consumption in KWh/Kg COD removed in time [Eq. (21)] was calculated using the following equation [40,46].

$$EEC = \frac{VIt}{\Delta COD^{*}vol} * \frac{1}{3600^{*}10^{-3}} \tag{21}$$

where V is the applied voltage, V; I is cell current, A; ΔCOD is the difference in initial and final COD concentration; vol is volume of the solution in L and t is time in s. Energy consumption at optimum condition is 0.0157 kWh/kg COD removal for latex processing wastewater and 0.0509 kWh/kg COD removal for latex production wastewater as presented in Figs. 4 and 5.

In order to ascertain the predicted models experiment was carried out at optimum conditions. The experimental values were found to agree with the predicted ones, with

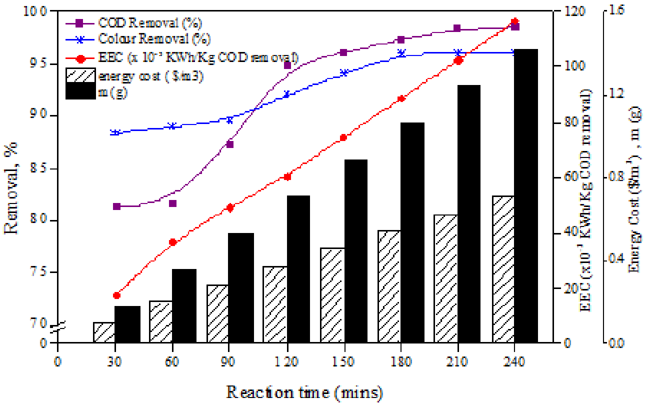

Fig. 4. COD removal, colour removal, EEC, mass of Fe^{2+} generated for Latex processing wastewater.

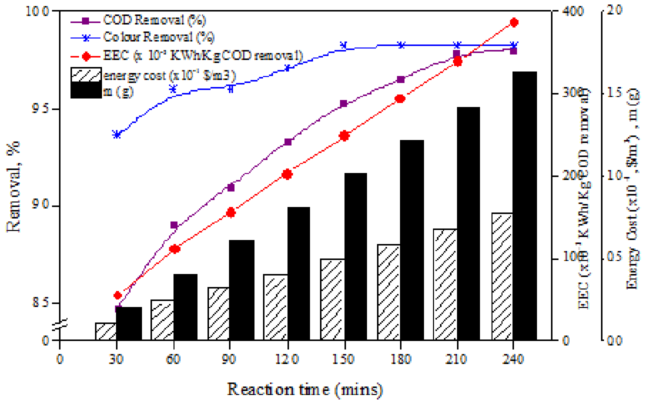

Fig. 5. COD removal, colour removal, EEC, mass of Fe^{2+} generated for Latex production wastewater.

COD and colour removal efficiencies of 81.25% and 90.50% for latex processing wastewater and in the case of latex production wastewater the values were 84.82% and 93.61% for 30 minutes of reaction time. Table 7 presents the experimental results under the optimum conditions compared with the simulated values from the proposed models [Eq. (10)–(13)]. These results substantiate that RSM is a powerful tool for optimizing the operational conditions of electro-Fenton for COD and colour removals.

3.4. Effect of reaction time and operational cost of electro-Fenton process

Experiment was conducted at optimal conditions to study the effect of reaction time to the extent of complete degradation. The decrease in COD with reaction time is shown in Figs. 4 and 5. As observed, COD removal increases sharply with the reaction time of 1–30 min, i.e. 20% to 81% for latex processing wastewater and 26% to 84% for latex production wastewater. The further increase of reaction time from 30 min resulted in gradual improvement of COD removal and about 98.5% of COD removal was attained in 210 min for latex processing wastewater and about 95% reduction in 150 min for latex production wastewater. Accordingly, the rate of reaction was rapid particularly at the beginning of the reaction because it may be due to the formation of hydroxyl radicals from the external addition of Fenton's reagents, after that it was suppressed considerably and attain a stage of recession at the end. The rate constant was almost equal to 0.01 min^{-1} for both waste waters. The corresponding colour removal at each time was measured and its removal is shown in Figs. 4 and 5. There was a noticeable reduction in colour initially up to 60 min and then reaches almost the same level due to the formation of ferric complexes when the time increases as shown in Figs. 4 and 5. It was noticed that the COD removal and colour removal have sharply increased up to 30 min and at the end of the treatment time the COD value was reduced to less than 250 mg/L and also the decolourization efficiency reaches to 96% for latex processing wastewater and 98% for latex production wastewater.

The operational cost is an important factor for the process, that it directly has an influence on the functioning of any treatment method. The degradation efficiency in terms of COD was carried out for both the wastewater at optimal conditions and operational cost [Eq. (22)] was estimated in terms of process cost and energy cost using the following formula [20].

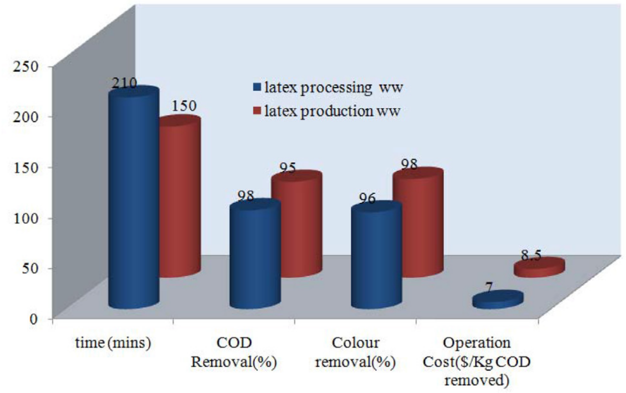

Fig. 6. Comparison of EF efficiencies for the removal of COD, colour and their operational costs at time for both the wastewater; (latex processing wastewater: H_2O_2 = 7424 mg/L, Fe^{2+} = 573 mg/L, current intensity = 0.34A) – (latex production wastewater: H_2O_2 = 3177 mg/L, Fe^{2+} = 378 mg/L, current intensity = 0.39 A).

$$\text{Operating Cost} = \text{process cost} + \text{energy cost} \tag{22}$$

where the process cost is the sum of product of chemical quantity required for 1 Kg of COD removal and its cost per kg and energy cost is electrical energy consumption (KWh/Kg COD removal) at particular time multiplied by its cost per kWh. Figs. 4 and 5 give a picture of energy cost for latex processing and production wastewater. The increase in time increases the operational cost since the energy cost is proportional with time. The operational cost for latex processing wastewater is 7 $/kg COD removal at 210 min and for latex production wastewater is 8.5 $/kg COD removal at 150 min. The highest removal efficiencies and operational costs of both the wastewater are illustrated in Fig. 6.

4. Conclusion

This study applied electro-Fenton process to oxidize latex wastewater and analyzed the significant role of pH, Fe^{2+}, H_2O_2 and current intensity through RSM. The highest COD removal (81.83%) and colour removal (91.47%) were achieved for latex processing wastewater at pH 3.5, Fe^{2+} 573 mg/L, H_2O_2 7424 mg/L and current intensity 0.34 A (16.04 A/m^2) and for latex production wastewater 85.12% of COD removal and 90.53% of colour removal were achieved at pH 4.1, Fe^{2+} 378 mg/L, H_2O_2 3170 mg/L and current intensity 0.39A (18.39 A/m^2).

From the results, both Latex waste waters were efficiently degraded with electro-Fenton process at an acidic pH of 3.5 and 4.1 and an optimal ratio of H_2O_2 and Fe^{2+} in the region of 13 and 9. The process under study provides

82% to 85% COD reduction in 30 min instead of long periods of chemical and biological treatments. The complete degradation of the process for latex wastewater attained at 150 min for latex processing wastewater and at 210 min for latex production wastewater with a cost of 7 $/kg COD removal and 8.5 $/kg COD removal respectively. On the whole, electro-Fenton process assures cost effective wastewater treatment in terms of achieving a low level of COD in the effluent for any latex wastewater which is acidic in nature at low energy consumption. Hence electro-Fenton process could become an effective alternative or additional process compared to conventional treatment system adopted in the industries. Overall, electro-Fenton process is a competent technology for applications in latex wastewater treatment.

References

[1] H.N. Nguyen, T.T. Luong, Situation of wastewater treatment of natural rubber latex processing in the Southeastern region, Vietnam, J. Viet. Environ., 2(2) (2012) 58–64.

[2] N.M. Mokhtar, W.J. Lau, A.F. Ismail, D. Veerasamy, Membrane distillation technology for treatment of wastewater from rubber industry in Malaysia, Procedia CIRP, 26 (2015) 792–796.

[3] H.P.J.S. Pillai, K. Girish, Rubber processing industry effluent treatment using a bacterial consortium, Int. J. Curr. Microbiol. App. Sci., 3(10) (2014) 775–782.

[4] W. Jawjit, P. Pavasant, C. Kroeze, Evaluating environmental performance of concentrated latex production in Thailand, J. Clean. Prod., 98 (2015) 84–91.

[5] W. Jawjit, C. Kroeze, S. Rattanapan, Greenhouse gas emissions from rubber industry in Thailand, J. Clean. Prod. ion, 18(5) (2010) 403–411.

[6] P. Tekasakul, S. Tekasakul, Environmental problems related to natural rubber production in Thailand, J. Aerosol Res., 21(2) (2006) 122–129.

[7] B. Sengupta, Development of standards for rubber products manufacturing industry, Comprehensive Industry Documents Series COINDS/67/2007, CPCB, Delhi - 32, pp.38.

[8] K.V.V.S. Kudaligama, P.A.J Yapa, Wastewater treatment in rubber industry with special emphasis on anaerobic systems, Bull. Rubber Res. Institute Sri Lanka, 48 (2007) 49–54.

[9] W. Worawit, L. Chih-Hsiang, T. Panote, K. Proespichaya, Characterization of organic substances in concentrated latex discharged effluent, Sixth PSU Eng. Conf., 2008.

[10] L. Ashok, S. Adishkumar, J.R. Banu, I.T. Yeom, Ferrioxalate-induced solar photo-Fenton treatment of natural rubber latex waste waters, Water Quality Res. J. Canada, 50(4) (2015) 349–358.

[11] K. Vijayaraghavan, D. Ahmad, A.Y.A. Yazid, Electrolytic treatment of Standard Malaysian Rubber process wastewater, J. Hazard. Mater., 150(2) (2008) 351–356.

[12] K. Vijayaraghavan, D. Ahmad, A.Y.A. Yazid, Electrolytic treatment of latex wastewater, Desalination, 219 (2008) 214–221.

[13] D. Tanikawa, K. Syutsubo, T. Watari, Y. Miyaoka, M. Hatamoto, S. Iijima, M. Fukuda, N.B. Nguyen, T. Yamaguchi, Greenhouse gas emissions from open-type anaerobic wastewater treatment system in natural rubber processing factory, J. Clean. Prod., 119 (2016) 32–37.

[14] Y. Wang, X. Li, L. Zhen, H. Zhang, Y. Zhang, C. Wang, Electro-Fenton treatment of concentrates generated in nanofiltration of biologically pretreated landfill leachate, J. Hazard. Mater., 229–230 (2012) 115–121.

[15] P. Ghosh, A.N. Samanta, S. Ray, Reduction of COD and removal of Zn^{2+} from rayon industry wastewater by combined electro-Fenton treatment and chemical precipitation, Desalination, 266 (2011) 213–217.

[16] O.T Can, COD removal from fruit-juice production wastewater by electro oxidation electro coagulation and electro-Fenton processes, Desal. Water Treat., 52(1–3) (2014) 65–73.

[17] R. Davarnejad, A. Sahraei, Industrial wastewater treatment using an electrochemical technique: an optimized process, Desal. Water Treat., 57(21) (2016) 9622–9634.

[18] P.V. Nidheesh, R. Gandhimathi, S.T. Ramesh, Degradation of dyes from aqueous solution by Fenton processes: a review, Environ. Sci. Pollut. Res., 20 (2013) 2099–2132.

[19] P.V. Nidheesh, T.S. Anantha Singh, Arsenic removal by electro coagulation process: Recent trends and removal mechanism, Chemosphere, 181 (2017) 418–432 .

[20] A.K. Abdessalem, N. Bellakhal, N. Oturan, M. Dachraoui, M.A. Oturan, Treatment of a mixture of three pesticides by photo and electro-Fenton processes, Desalination, 250 (2010) 450–455.

[21] E. Rosales, O. Iglesias, M. Pazos, M.A. Sanroman, Decolourisation of dyes under electro-Fenton process using Fe alginate gel beads, J. Hazard. Mater., 213–214 (2012) 369–377.

[22] Y. Fan, Z. Ai, L. Zhang, Design of an electro-Fenton system with a novel sandwich film cathode for wastewater treatment, J. Hazard. Mater., 176 (2010) 678–684.

[23] G. Varank, S.Y. Guvenc, G. Gurbuz, G.O. Engin, Statistical optimization of process parameters for tannery wastewater treatment by electro coagulation and electro-Fenton techniques, Desal. Water Treat., 57(53) (2016) 25460–25473.

[24] K. Ulucan, U. Kurt, Comparative study of electrochemical wastewater treatment processes for bilge water as oily wastewater: a kinetic approach, J. Electroanal. Chem., 747 (2015) 101–111.

[25] W.P. Ting, M.C. Lu, Y.H. Huang, Kinetics of 2,6-dimethylaniline degradation by electro-Fenton process, J. Hazard. Mater., 161(2–3) (2009) 1484–1490.

[26] C.C. Su, A.T. Chang, L.M. Bellotindos, M.C. Lu, Degradation of acetaminophen by Fenton and electro-Fenton processes in aerator reactor, Sep. Purif. Technol., 99 (2012) 8–13.

[27] H.O. Vargas, N. Oturan, M.A. Oturan, E. Brillas, Electro-Fenton and solar photo electro-Fenton treatments of the pharmaceutical ranitidine in pre-pilot flow plant scale, Sep. Purif. Technol., 146 (2015) 127–135.

[28] APHA-AWWA-WEF, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, McGraw-Hill, Washington, DC, 2005.

[29] P. Aswathy, R. Gandhimathi, S.T. Ramesh, lectrocoagulation process, Sep. Purif. Technol., 159 (2016) 108–115.

[30] O.P. Sahu, P.K. Chaudhari, Electrochemical treatment of sugar industry wastewater: COD and color removal, J. Electro anal. Chem., 739 (2015) 122–129.

[31] Omorusi, V. Irogue, Evaluation of wastewater (effluent) from rubber latex concentrate for microbiological and physico chemical properties, Researcher, 5(5) (2013) 60–63.

[32] M. Umar, H.A. Aziz, M.S. Yusoff, Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate, Waste Manage., 30 (2010) 2113–2121.

[33] Y. Wang, Y. Liu, T. Liu, S. Song, X. Gui, P. Tsiakaras, Dimethyl phthalate degradation at novel and efficient electro-Fenton cathode, Appl. Catal. B: Environ., 156–157 (2014) 1–7.

[34] C.T. Wang, W.L. Chou, M.H. Chung, Y.M. Kuo, COD removal from real dyeing wastewater by electro-Fenton technology using an activated carbon fiber cathode, Desalination, 253 (2010) 129–134.

[35] P.V. Nidheesh, R. Gandhimathi, Trends in electro-Fenton process for water and wastewater treatment: An overview, Desalination, 299 (2012) 1–15.

[36] S. Kourdali, A. Badis, A. Boucherit, Degradation of direct yellow 9 by electro-Fenton: Process study and optimization and, monitoring of treated water toxicity using catalase, Ecotoxicol. Environ. Safety, 110 (2014) 110–120.

[37] P.V. Nidheesh, R. Gandhimathi, Electrolytic removal of Rhodamine B from aqueous solution by peroxi coagulation process, Environ. Sci. Pollut. Res., 21 (2014) 8585–8594.

[38] N. Masomboon, C. Ratanatamskul, M.C. Lu, Chemical oxidation of 2,6-dimethylaniline by electrochemically generated Fenton's reagent, J. Hazard. Mater., 176 (2010) 92–98.

[39] D. Venu, R. Gandhimathi , P.V. Nidheesh, S.T. Ramesh, Treatment of stabilized landfill leachate using peroxicoagulation process, Sep. Purif. Technol., 129 (2014) 64–70.

[40] A. Babuponnusami, K. Muthukumar, Advanced oxidation of phenol: A comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes, Chem. Eng. J., 183 (2012) 1–9.

[41] K. Thirugnanasambandham, S. Kandasamy, V. Sivakumar, R.K. Kumar, R. Mohanavelu, Modeling of by-product recovery and performance evaluation of Electro-Fenton treatment technique to treat poultry wastewater, J. Taiwan Inst. Chem. Eng., 46 (2015) 89–97.

[42] S. Mohajeri, H.A. Aziz, M.H. Isa, M.A. Zahed, M.N. Adlan, Statistical optimization of process parameters for landfill leachate treatment using electro-Fenton technique, J. Hazard. Mater., 176 (2010) 749–758.

[43] P.V. Nidheesh, R. Gandhimathi, Effect of solution pH on the performance of three electrolytic advanced oxidation processes for the treatment of textile wastewater and sludge characteristics, RSC Adv., 4 (2014) 27946 –27954.

[44] J.A. Banuelos, A. El-Ghenymy, F.J. Rodriguez, J. Manriquez, E. Bustos, A. Rodriguez, E. Brillas, L.A. Godinez, Study of an air diffusion activated carbon packed electrode for an electro-Fenton wastewater treatment, Electrochim. Acta, 140 (2014) 412–418.

[45] R. Davarnejad, M. Mohammadi, A.F. Ismail, Petrochemical wastewater treatment by electro-Fenton process using aluminum and iron electrodes: Statistical comparison, J. Water Process Eng., (2014) 18–25.

[46] K. Godini, G. Azarian, A.R. Rahmani, H. Zolghadrnasab, Treatment of waste sludge: a comparison between anodic oxidation and electro-Fenton processes, J. Res. Health Sci., 13(2) (2013) 188–193.